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I also certify that by virtue of an assignment registered under the Patents Act 1977, the application is now proceeding in the name as substituted.

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Signed Andrew Gersey

Dated 3 November 1999

GB9823081.6

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of

DEVRO PLC
Modiesburn
Chryston
GLASGOW
G69 0JE
United Kingdom

Incorporated in the United Kingdom

[ADP No. 07054794001]

FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG E.V.
Leonrodstrasse 54
80636 Munich
Federal Republic of Germany

[ADP No. 07417058002]

Patents Form 1/77

Pate... Act 1977
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1/77

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Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference — DCM/ED/P08467GB

2. Patent application number *(The Patent Office will fill in this part)* — 21 OCT 1998 — **9823081.6**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Devro plc
Moodiesburn
Chryston
Glasgow G69 0JE

SECTION 30 (1977 ACT) APPLICATION FILED 16.4.99

Patents ADP number *(if you know it)* — 7054794001

If the applicant is a corporate body, give the country/state of its incorporation — Scotland, United Kingdom

4. Title of the invention — Cellulose Extrusion

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Cruikshank & Fairweather
19 Royal Exchange Square
Glasgow G1 3AE

Patents ADP number *(if you know it)* — 547002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* — Yes

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	6
Claim(s)	1
Abstract	–
Drawing(s)	1

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date

CRUIKSHANK & FAIRWEATHER 20 October 1998

12. Name and daytime telephone number of person to contact in the United Kingdom

D C MacDougall
0141 221 5767

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DEVROPEL - N2 BLANKET
29 September 1998

CELLULOSE EXTRUSION

The present invention relates to a process for extruding a solution of cellulose, water and an amine oxide according to the well known amine oxide extrusion process. In particular, it relates to the reduction or avoidance of degradation or discolouration of the extruded cellulose solution, which otherwise leads to poor product quality.

The production of extruded cellulose articles, such as fibres, sheets or tubes has been known for more than a century. In this so called "viscose" process cellulose is derivatised with carbon disulphide and solubilised in diluted sodium hydroxide to form a solution and the solution is extruded. The extruded cellulose is then regenerated and reverts to its solid form. The viscose process has been used for the manufacture of sausage casings, flat cellophane films, rayon fibres, bottle caps etc. A disadvantage of the viscose process is that it employs carbon disulphide CS_2 as an intermediate. The use of CS_2 is environmentally undesirable.

More recently, the so called "amine-oxide" process has been developed wherein the cellulose is dissolved in a mixture of water and an amine-oxide solvent. A commonly used amine-oxide solvent is the tertiary amine-oxide NMMO (N-methyl morpholine N-oxide). This solvent is able to dissolve cellulose without having to first derivatise the

cellulose, as for example in the viscose process. Once solubilised the cellulose will precipitate from the solution as a regenerated cellulose product by contacting the solution with a precipitation liquid which is a non-solvent for cellulose and a solvent for NMMO. The most frequently used precipitation liquid for the amine-oxide process is water.

Prior to extrusion, the cellulose amine-oxide solution may be heated to a temperature of around 100°C. Thermal stabilisers, such as propyl galate, may be added to the solution to inhibit the thermal degradation of NMMO. However, it has been found when extruding cellulose films, that the extruded material was coloured brown-red. Moreover, the colour intensity varied between different extrusion runs in an apparently uncontrolled manner. Colour variation could even be observed during a single long extrusion run.

It is an object of the present invention to mitigate these problems.

The present invention provides a process for extruding a solution of cellulose, water and an amine-oxide, which comprises

- providing a closed vessel containing said cellulose solution;
- providing an inert gas blanket above the cellulose solution in the vessel; and
- delivering the cellulose solution to an extrusion means for extrusion thereof.

Thus, it has been surprisingly found that protecting the stored cellulose solution from oxidation by the provision of an inert gas blanket substantially mitigates against undesirable colour variations in the extruded product. Generally, the inert gas is nitrogen but other inert gases capable of protecting against oxidation might also be used.

The cellulose solution for extrusion comprises water and an amine-oxide. Suitable amine-oxides are known in the art and are particularly tertiary amine-oxides, such as NMMO (N-methyl morpholine N-oxide). Generally, cellulose pulp is mixed with an aqueous amine-oxide solution containing about 50% NMMO. The cellulose is unable to dissolve at such high water content. The water is then removed from the mixture by applying heat and reduced pressure. Typically, the pressure is set so the water boils off at approximately 70°C and the vapours are removed and recovered by re-condensation. Once the water content has been reduced from about 50% to about 12%, the NMMO mono hydrate is formed and the cellulose dissolves therein. The temperature is then typically increased to around 95°C to completely dissolve all the cellulose fibres. The reduced pressure is maintained or increased in order to remove any remaining air bubbles from the cellulose solution. This solution is then suitable for extrusion.

The solution may be extruded directly or stored for prolonged periods without detrimental effects. Furthermore, the solution may be solidified by decreasing

the temperature (from around 100°C) to allow the solution to solidify and then ground to form pellets.

The cellulose solution ready for extrusion is stored in the closed vessel, which enables a blanket of inert gas to be maintained in the free space above the cellulose solution. The inert gas may be slightly pressurised in order to reduce ingress of air from outside the vessel, which might lead to deterioration of the stored cellulose solution. The use of a positive pressure of inert gas may also be of assistance in delivering the cellulose solution to the extrusion means.

The cellulose solution is extruded via the extrusion means into any desired shape, such as flat sheets or tubes. The process is particularly applicable to the production of wrappings or tubular casings for sausages, salami or other cased food products. The cellulose casing may be either used during the production of the food product and removed thereafter or may be retained in place.

Embodiments of the present invention will now be described by way of example only with reference to the attached Figure 1 and the Example.

Figure 1 illustrates schematically appparatus for extruding a cellulose amine-oxide aqueous solution comprising a cellulose storage vessel 0 containing a cellulose amine-oxide solution 1 protected in the free space 2 above by a blanket of nitrogen at a slightly above-atmospheric pressure. The cellulose solution is fed to an extruder screw 5 driven by an extruder drive 4 and is then

delivered by a gear pump 8 into an extrusion head 3. The cellulose amine-oxide solution is extruded in the form of a tube 6 via an air gap into a precipitation liquid 7 (for example water). The extruded tube is then finished in conventional manner.

Example

A cellulose solution for extrusion was prepared by mixing cellulose pulp with an aqueous NMMO solution containing about 50% by weight NMMO. Water was removed from the mixture by applying heat and a reduced pressure. The water boiled off at approximately 70°C and the vapours were recovered in a condensor. Once the water content had been reduced to about 12%, the NMMO monohydrate formed and the cellulose began to dissolve in the NMMO monohydrate solution. A stabiliser was added to the solution to inhibit thermal degradation of NMMO. The temperature was then increased to about 95°C and all the cellulose fibres dissolved to form an extrusion solution. The pressure was further reduced to remove air bubbles from the cellulose solution. At a temperature of about 100°C the cellulose solution is a visco-elastic melt with a high viscosity and a pronounced elastic behaviour. The time to produce the cellulose solution was about 3 hours.

The cellulose solution was then stored in a storage vessel such as shown in Figure 1 and extruded through an annular die so as to form a NMMO-cellulose tube. The tube was passed into a percipitation bath containing a

percipitation medium, such as water or aqueous NMMO solution. A positive pressure is applied into the air gap between the extrusion die and the precipitation bath so as to keep the tube inflated up. The inner volume of the tube is also kept filled up with precipitation liquid, the composition of which is controlled to be constant.

In the absence of a nitrogen blanket above the cellulose solution in the storage vessel, it was frequently noticed that the extruded tube was coloured brown-red and that the colour intensity varied between different extrusion runs. Moreover, even during a single extrusion run of 20 minutes the colour changed from light-red at the beginning of the run to dark brown-red at the end. However, when a nitrogen blanket was employed in the storage vessel according to the present invention, the amount of discolouration was reduced. Moreover, the pressurised nitrogen enhanced filling of the extruder screw.

Claims

1. A process for extruding a solution of cellulose, water and an amine-oxide, which comprises

- providing a closed vessel containing said cellulose solution;
- providing an inert gas blanket above the cellulose solution in the vessel; and
- delivering the cellulose solution to an extrusion means for extrusion thereof.

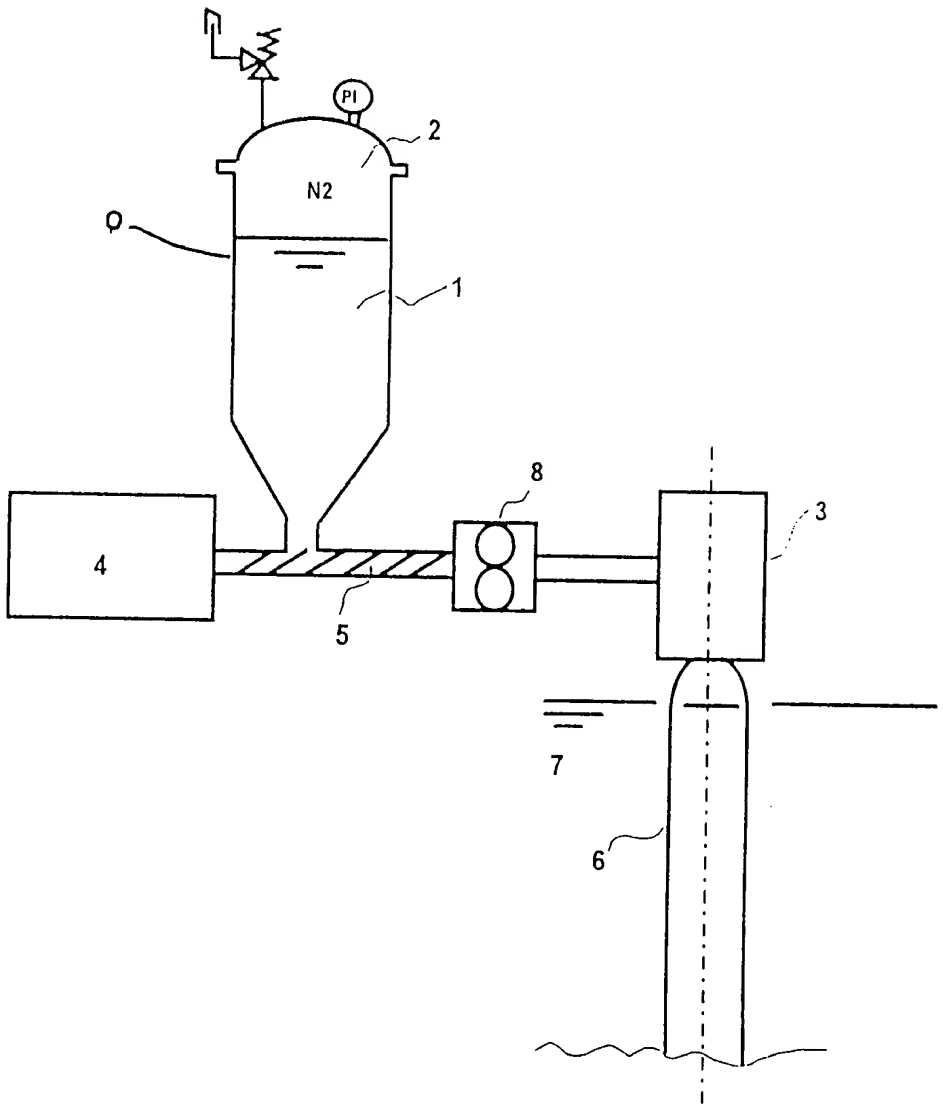

FIGURE 1 : NITROGEN BLANKET ON TOP OF MELTED DOPE IN EXTRUDER FEEDER HOPPER

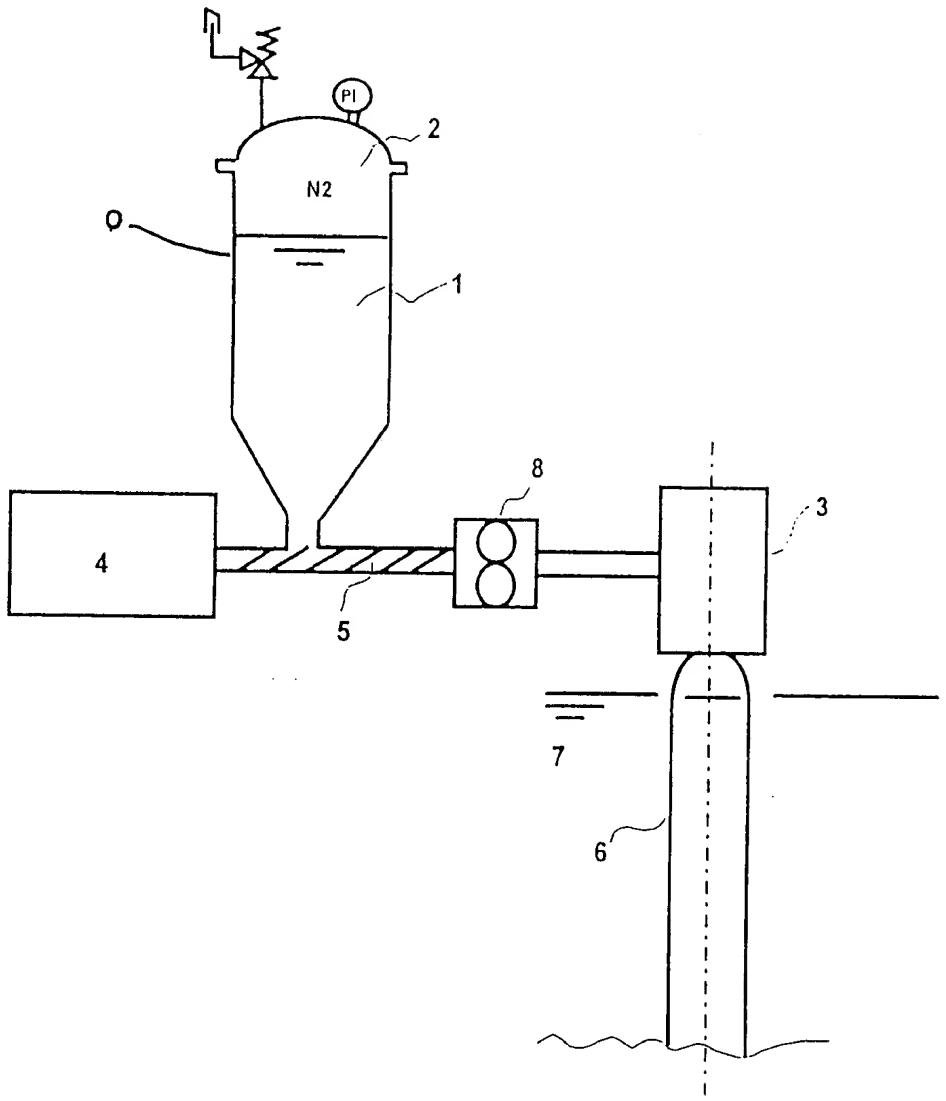

FIGURE 1 : NITROGEN BLANKET ON TOP OF MELTED DOPE IN EXTRUDER FEEDER HOPPER